Journal of Molecular Catalysis A: Chemical 180 (2002) 141–159

www.elsevier.com/locate/molcata

The role of bismuth as promoter in Pd–Bi catalysts for the selective oxidation of glucose to gluconate

Mireille Wenkin [a], Patricio Ruiz [b], Bernard Delmon [b], Michel Devillers [a,*]

[a] *Unité de Chimie des Matériaux Inorganiques et Organiques, Université Catholique de Louvain,*
Place Louis Pasteur 1/3, B-1348 Louvain-la-Neuve, Belgium
[b] *Unité de Catalyse et de Chimie des Matériaux Divisés, Université Catholique de Louvain,*
Place Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

Received 8 June 2001; received in revised form 16 August 2001; accepted 17 October 2001

Abstract

Bismuth is a well-established promoter of noble metal-based catalysts for the selective liquid phase oxidation of alcohols, aldehydes and carbohydrates with molecular oxygen. Experiments were carried out to improve the understanding of the promoting role of bismuth in bimetallic Pd–Bi catalysts used for the selective oxidation of glucose to gluconate. In relationship with the fact that these catalysts undergo substantial bismuth leaching under the reaction conditions, particular attention was paid to the possible role played by the soluble fraction of bismuth in the oxidative process. Carbon-supported Pd–Bi/C catalysts characterized by various Bi–Pd compositions ($0.33 \leq \mathrm{Bi/Pd} \leq 3.0$, 10 wt.%Pd + Bi) were prepared from acetate-type precursors, tested under various experimental conditions and analyzed by X-ray diffractometry and X-ray photoelectron spectroscopy (XPS). Whatever the initial catalyst composition, the surface intensity ratio measured by XPS in used catalysts lies in the range 0.4–0.6, suggesting that the dynamic state of the catalyst involves the association of one Bi and two to three Pd atoms. The leaching process and the promoting effect itself are discussed in line with the formation of Bi–glucose and Bi–gluconate complexes present in solution but also as adsorbed species at the catalyst surface. The performances of a monometallic Pd/C catalyst are significantly improved in the presence of adequate amounts of soluble Bi. The involvement of the soluble fraction of bismuth in the overall mechanistic scheme of glucose oxidative dehydrogenation is suggested. The detrimental effect of large amounts of soluble bismuth is attributed to a too extensive adsorption of Bi–glucose complexes on the surface Pd atoms. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bismuth; Oxidation; Deactivation; Glucose; Gluconate

1. Introduction

The liquid phase oxidation of alcohols and aldehydes, with molecular oxygen, in the presence of promoted Pd/C and Pt/C catalysts has been extensively studied in the last decade [1–3,54]. Lead and bismuth are the most common promoters but many others including Cd, Tl, Ag, Te, Se, Co, Ce and Sn have been proposed [4–7]. When used alone, these elements are inactive for the concerned oxidation reactions, but when associated with the noble metal, they considerably increase the overall catalytic performances (activity, sometimes selectivity) and/or the lifetime of the catalysts. The origin of the promoting role of bismuth on the activity of Pd or Pt is still a matter of discussion. Among various interpretations, the most

---

[*] Corresponding author. Tel.: +32-10-47-2827;
fax: +32-10-47-2330.
E-mail address: devillers@chim.ucl.ac.be (M. Devillers).

1381-1169/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(01)00421-6

currently mentioned refer to: (i) geometric blocking effects of active sites centered on the noble metal [8–12], (ii) the formation of new active centers [4,8,13], (iii) the lowering of Pt metal corrosion in acidic media [14,15], (iv) the stabilization of the metallic state of Pt [6] and (v) the formation of surface complexes between the promoting element and substrates displaying chelating properties [10,16–19]. However, Heinen et al. [20] reported also the detrimental effect of catalyst promotion in the case of Bi–Pt/C catalysts engaged in fructose oxidation: deactivation of the promoted catalysts is more extensive than that of the unpromoted one, but the presence of Bi has a positive effect on the selectivity to 2-ketogluconic acid. A reverse situation was reported by Brönnimann et al. [21] in the oxidation of L-sorbose to 2-keto-L-gulonic acid: promotion of Pt or Pd by small amounts of Bi or Pb was shown to increase the initial conversion rate, but simultaneously to decrease the selectivity and the maximum obtainable yield. The engineering aspects of these noble metal catalyzed processes were recently analyzed by Kluytmans et al. [22].

During the past few years, we dedicated a research programme to the preparation and characterization of carbon-supported bimetallic catalysts Pd–Bi/C obtained according to several experimental procedures, and to the investigation of their catalytic performances towards the selective reaction of molecular oxygen with glucose to generate gluconic acid [23–25]. These earlier studies demonstrated the influence of the carboxylate group on the catalytical properties, the losses of bismuth from the catalysts during the catalytic tests due to the chelating properties of glucose and gluconate and the presence of Bi–Pd intermetallic compounds [$BiPd–BiPd_3–Bi_2Pd$] in the active phase of the supported bimetallic catalysts.

In order to investigate the role played by the various Bi–Pd intermetallic compounds in the catalytic process, bimetallic Pd–Bi/C catalysts with different Bi/Pd ratios and Bi_xPd_y intermetallics whose presence was suspected in the above catalysts were prepared and tested in the glucose oxidation reaction [23]. The catalytic performances of supported Pd–Bi/C catalysts and the Bi losses from the catalysts during operation were both found to be highly dependent upon the composition of the active phase. Furthermore, Bi losses increase with the Bi content, but without any clear relationship with the catalytic activity. The experiments performed with the pure intermetallics Bi_2Pd, BiPd and $BiPd_3$ showed that the intrinsic catalytic behaviors of these phases were very different; the most active phase, Bi_2Pd, is the one that loses the largest amount of Bi, whereas $BiPd_3$, the most stable phase during operation, remains totally inactive.

Although, there seems to be no simple relationship between the extent of Bi dissolution and the catalytic performances, partial leaching of the promoting element seems to be a key feature for their functioning [25]. The present paper describes complementary experiments carried out to improve the understanding of the promoting role of bismuth in these catalysts. More particularly, experiments devoted to the possible role played by the soluble fraction of bismuth in the oxidative process were conducted. This was measured by monitoring glucose oxidation with a monometallic Pd/C catalyst in the presence of dissolved bismuth. The following questions will be addressed: (i) What are the consequences of Bi dissolution on the surface characteristics of the bimetallic catalysts? (ii) Can the solubilized fraction of bismuth play a role in the catalytic process? (iii) Is bismuth leaching related to or responsible for the deactivation of these catalysts? Because Bi leaching was shown to be a time-dependent process, the surface state of several bimetallic catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) after their use in reaction conditions for long periods, in either the continuous or the discontinuous mode.

The role of the bismuth present in the active phase of the catalyst and the optimal Bi/Pd composition of the active sites were also investigated. From the catalytic performances of several bimetallic Pd–Bi/C catalysts ($0.33 < \text{molar ratio Bi/Pd} < 3$) for the above reaction under different conditions, and from the catalysts characterization results (XPS and X-ray diffractometry (XRD)), an optimal Bi/Pd composition of the active sites can be suggested.

Finally, because there is no doubt that the presence of chelating agents like gluconate but also glucose is a critical aspect which governs and explains the stabilization of Bi as soluble species in the reaction medium, a section of this paper will be specifically dedicated to a comprehensive view of the Bi–glucose and Bi–gluconate complexes according to the related coordination chemistry literature on this topic.

2. Experimental

2.1. Catalyst supports

The activated carbons used as supports are supplied by NORIT. They correspond to the trade names SX_{plus} ($S_{BET} = 1000\,m^2\,g^{-1}$—usual selected particle size = 100–200 μm, exceptionally 50–100 μm) and PKDA 10X30 ($S_{BET} = 550\,m^2\,g^{-1}$—selected particle size = 50–100 μm). They are noted hereafter C_{SX} and C_0, respectively.

2.2. Metallic precursors

Palladium(II) acetate (ACROS, 47.5% Pd) and bismuth(III) nitrate pentahydrate (p.a., Fluka) were used as received. Bismuth(III) oxoacetate, $BiO(O_2CCH_3)$, was obtained by adding 5 ml acetic acid (99.5%) to a suspension of 5 g of Bi_2O_3 (ACROS, 99.9%) in 100 ml acetone. The mixture was refluxed for 6 h, the precipitate was filtered, washed with acetone and ether, then air dried at room temperature.

2.3. Catalyst preparation

2.3.1. Monometallic Pd/C (5 wt.%) and Bi/C (5 or 10 wt.%) catalysts

Palladium(II) acetate or bismuth(III) oxoacetate was dispersed in the presence of 7.2 g of activated carbon in 250 ml *n*-heptane (ACROS, 99+%) under ultrasonic stirring for 30 min. The hydrocarbon was evaporated very slowly under reduced pressure at room temperature and the precursor deposited on the support was decomposed upon heating under nitrogen at 500 °C during 18 h. These catalysts were coded Pd/C_{SX}, Bi/C_{SX}, Pd/C_0 and Bi/C_0.

2.3.2. Bimetallic Pd–Bi (Pd + Bi = 10 wt.%)/C catalysts

Six carbon-supported bimetallic catalysts characterized by different bulk Bi/Pd molar ratios but a constant metal/catalyst weight percentage of 10 were prepared according to experimental conditions similar to those described above for the monometallic catalysts. The Bi–Pd compositions selected correspond to the following values of the Bi/Pd molar ratio: 0.33, 0.4, 0.5, 1.0, 2.0 and 3.0. These catalysts were coded, respectively, as **3**Pd**1**Bi/C_0, **5**Pd**2**Bi/C_0, **2**Pd**1**Bi/C_0, **1**Pd**1**Bi/C_0, **1**Pd**2**Bi/C_0, and **1**Pd**3**Bi/C_0, the numbers preceding Pd and Bi referring to the relative molar amount. Taking into account the differences in atomic masses between both elements, these compositions approximately correspond to the Pd and Bi weight percentages indicated in parentheses after the following symbols: Pd(6.0)–Bi(4.0), Pd(5.6)–Bi(4.4), Pd(5.0)–Bi(5.0), Pd(3.4)–Bi(6.6), Pd(2.0)–Bi(8.0) and Pd(1.5)–Bi(8.5). They were prepared by deposition from a slurry of Pd(II) acetate and Bi(III) oxoacetate particles in *n*-heptane, according to the following procedure. The adequate amount of palladium acetate was dispersed in the presence of the activated carbon (2.7 g) in about 100 ml *n*-heptane under ultrasonic stirring for 30 min. After slow evaporation of the solvent at room temperature under reduced pressure, the appropriate amount of bismuth oxoacetate was deposited on the obtained monometallic catalyst according to the same procedure. The bimetallic catalyst was then activated by thermal heating under nitrogen at 500 °C during 18 h.

2.4. Measurement of the catalytic performances

2.4.1. Reactor vessel

The selective oxidation of D-glucose into gluconic acid was carried out at atmospheric pressure in a 600 ml flat bottom double-wall glass reactor. The temperature was controlled through water circulation. Constant thorough mixing of the reaction medium was ensured by a mechanical stirrer (HEIDOLPH RZR 2051). The pH of the reaction mixture was measured continuously by a combined glass-reference electrode (BECKMAN model 39843) coupled with a pH meter/controller (METROHM, Stat Titrino 718). To maintain a constant pH (9.25–9.45) in the reaction mixture during operation, the sugar-derived carboxylic acids formed were neutralized by adding a 20 or 40 wt.% aqueous solution of sodium hydroxide. The base consumption was recorded as function of time.

2.4.2. Standard oxidation procedure

The glucose solution (72 g glucose (99+%, ACROS) in 400 ml water) was heated in the reactor to 50 °C. Once the temperature was stabilized, the catalyst was added to the solution and the oxidation reaction started by introducing oxygen (flow rate: 0.4 l min^{-1}) in the stirred (1000 rpm) slurry. The catalytic tests were interrupted after 4 h, and the catalyst was removed from the reaction mixture by filtration. The filtrate was then analyzed by ^{13}C-NMR and atomic absorption spectrometry. The catalyst was washed with water, dried under vacuum and analyzed by XPS and XRD.

Three series of tests were carried out with the bimetallic **X**Pd**Y**Bi/C_0 catalysts: at constant catalyst weight, or by changing the catalyst weight in order to keep either the palladium weight, or the bismuth weight constant. Depending on the Bi–Pd composition, the amounts used in the catalytic tests were in the range 32–133 mg. Measurements performed under these conditions with different stirring rates (in the range 1000–1800 rpm) confirmed the absence of external diffusional limitations.

As described recently by Kluytmans et al. [22], when performing these experiments, particular attention has to be paid to the safety aspects related to possible explosions, as a consequence of the H_2 evolution and the subsequent eventuality that the resulting H_2/O_2 mixture exceeds the explosion limits. Although, no trouble was observed under the experimental conditions described above, this warning should be kept in mind whenever such experiments are scaled up to a larger size or carried out in different reaction conditions, particularly if higher catalyst amounts are used.

2.4.3. Experiments in the presence of dissolved bismuth

A monometallic catalyst, Pd/C_{SX}, was also tested in the presence of dissolved bismuth according to the following procedure: a glucose oxidation run was started with X mg of a Bi-based monometallic catalyst under the standard conditions described in Section 2.4.2. After a certain time, the catalyst was removed from the reaction medium by filtration and water was added to the filtrate to reach a volume of 500 ml. The solution was then analyzed by atomic absorption spectrometry to determine its bismuth content. Four-hundred and fifty milliliter of the previous solution were then heated in the reactor at 50 °C. Once the temperature was stabilized, the Pd-based monometallic catalyst (54 mg) was added to the solution and the oxidation reaction was started by introducing oxygen (flow rate: 0.4 l min^{-1}) in the stirred (1000 rpm) slurry. The catalytic tests were interrupted after 4 h.

2.4.4. Analysis of the reaction medium

The composition of the reaction mixture was determined by ^{13}C-NMR. The spectra were measured under standard conditions on a BRUKER AM500 spectrometer equipped with a computer Aspect 3000, using a 5 mm ^1H probe at 25 °C. D_2O solvent was used as an internal deuterium lock signal with the methyl carbons of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal spectral reference.

The bismuth and palladium losses from the catalysts in the reaction mixture during the catalytic tests were determined by analyzing the collected filtrates by atomic absorption spectrometry using a spectrometer Perkin Elmer 3110 equipped with a flame atomizer.

2.4.5. Expression of the catalytic results

The ^{13}C-NMR analyses confirmed that gluconic acid was the only carboxylic acid generated in the reaction medium. Therefore, the yields in gluconic acid were calculated directly from the NaOH consumption. The main side product was fructose resulting from glucose isomerization, but its yield never exceeded 8%.

2.5. Catalyst characterization techniques

2.5.1. XRD

Powder X-ray diffraction patterns were obtained with a Siemens D-5000 diffractometer using the Cu Kα radiation ($\lambda = 154.18$ pm). The samples were analyzed after deposition on a quartz monocrystal sample-holder supplied by Siemens. The crystalline phases were identified by reference to the JCPDS data files.

2.5.2. XPS

XPS was performed on an SSI-X-probe (SSX-100/206) spectrometer from Fisons, using the Al Kα radiation ($E = 1486.6$ eV). The energy scale was calibrated by taking the Au $4f_{7/2}$ binding energy at 84 eV. The C 1s binding energy of contamination carbon set at 284.8 eV was used as internal standard value. The analyses of bismuth and palladium were based on the Bi $4f_{7/2}$ and Pd $3d_{5/2}$ photopeaks. The intensity ratios $I(\text{Bi } 4f_{7/2})/I(\text{Bi } 4f_{5/2})$ and $I(\text{Pd } 3d_{5/2})/I(\text{Pd } 3d_{3/2})$ were fixed at 1.33 and 1.5, respectively.

2.5.3. Scanning electron microscopy coupled to energy-dispersive X-ray analysis (SEM-EDX)

SEM images of the supported catalysts were obtained from secondary and backscattered electron intensities, measured with a electron microscope LEICA under a voltage of 25 kV. The samples were deposited onto an aluminum support from a slurry in acetone. After being dried at room temperature under normal pressure, they were analyzed without previous metallization. Energy-dispersive analyses were based on the M_α and M_β rays of Bi, and the $L_{\alpha1}$ and $L_{\alpha2}$ rays of Pd.

3. Results

3.1. Catalytic results

3.1.1. Comparison of the activity of mono- and bimetallic catalysts

The catalytic performances of monometallic Pd/C and bimetallic Pd–Bi/C catalysts obtained by different preparative methods and various Pd and Bi precursors have already been compared in a previous paper [23]. Four typical experiments are compared in Fig. 1. It is noteworthy that the promoting influence of Bi does not require its presence in the form of a bimetallic catalyst. An increase in gluconic acid production is observed when two monometallic Pd/C and Bi/C catalysts are used simultaneously. However, for identical metal amounts, the yields obtained in this case remain smaller than when a bimetallic Pd–Bi/C catalyst is used.

3.1.2. Influence of the bulk Bi/Pd molar ratio

Three series of catalytic tests were carried out by keeping the catalyst weight ($m_{\text{cat}} = 54$ mg), the palladium weight ($m_{\text{Pd}} = 2.7$ mg) or the bismuth weight ($m_{\text{Bi}} = 2.7$ mg) constant. The results of the first series, at constant catalyst mass, are listed in Table 1. Yields in gluconic acid (line 3) and the extent of bismuth dissolution in the reaction medium (lines 4 and 5) are given after 4 h running. The bismuth losses are expressed as percentages of the initial bismuth loading of the catalyst. The dependence of the yield in gluconic acid and of the Bi losses with respect to the catalyst composition, characterized by the bulk Bi/Pd molar ratio, is illustrated in Fig. 2a–c, for the experiments carried out at constant Pd mass, Bi mass and catalyst mass, respectively.

Possible ways to evaluate the performances of these catalysts are to compare the yields in gluconic acid with the total amount of catalysts (line 7) or the total amount of palladium (line 9). When the first option is selected, variations are relatively small and just indicate that synergy occurs between bismuth and palladium. When using the second activity rating (line 9), a maximum clearly appears around the composition characterized by the molar ratio $\text{Bi}/\text{Pd} = 1$. The promoter role of bismuth appears more evidently in the range $0.33 < \text{Bi}/\text{Pd} < 1.0$, namely for Bi amounts lower than those corresponding to $\text{Bi}/\text{Pd} = 1.0$, with a clear increase when this ratio changes from 0.33 to 1.0 (line 9). The objective of the present work being to investigate the respective roles of dissolved and residual Bi, the yields can also be compared with the corresponding amounts (lines 10 and 11). The highest

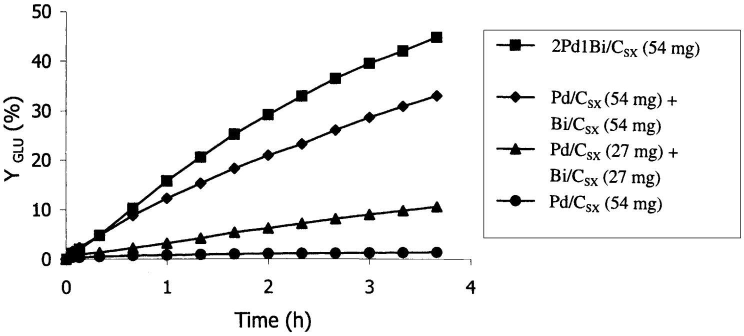

Fig. 1. Compared yields in gluconic acid vs. time for a monometallic Pd/C_{SX}, a bimetallic **2**Pd**1**Bi/C_{SX}, and a mixture of two monometallic Pd/C_{SX} and Bi/C_{SX} catalysts (standard reaction conditions).

Table 1
Catalytic performances and Bi losses of carbon-supported Bi–Pd catalysts engaged in catalytic tests with a constant catalyst mass (54 mg) (reaction conditions: 72 g glucose, 400 ml water, pH 9.25–0.4 l O_2/min, 50 °C, 1000 rpm, 4 h)

		3Pd**1**Bi/C_0 (Bi/Pd = 0.33)	**5**Pd**2**Bi/C_0 (Bi/Pd = 0.4)	**2**Pd**1**Bi/C_0 (Bi/Pd = 0.5)	**1**Pd**1**Bi/C_0 (Bi/Pd = 1)	**1**Pd**2**Bi/C_0 (Bi/Pd = 2)
1	Bi engaged (mg)	2.1	2.4	2.7	3.6	4.3
2	Pd engaged (mg)	3.3	3.0	2.7	1.8	1.1
3	Y_{GLU} (%)	26	23	30	38	17
4	Bi losses (%)	12	9	32	37	63
5	Bi dissolved (mg)	0.25	0.22	0.86	1.33	2.71
6	Bi residual (mg)	1.85	2.18	1.84	2.27	1.59
7	$Y_{\mathrm{GLU}}/m_{\mathrm{cat}}$ (%/mg)	0.5	0.4	0.6	0.7	0.3
8	$Y_{\mathrm{GLU}}/m_{\mathrm{Bi}}$ engaged (%/mg)	12.4	9.6	11.1	10.6	4.0
9	$Y_{\mathrm{GLU}}/m_{\mathrm{Pd}}$ engaged (%/mg)	7.9	7.7	11.1	21.1	15.5
10	$Y_{\mathrm{GLU}}/m_{\mathrm{Bi}}$ dissolved (%/mg)	103.2	106.5	34.7	28.5	6.3
11	$Y_{\mathrm{GLU}}/m_{\mathrm{Bi}}$ residual (%/mg)	14.1	10.5	16.3	16.8	10.7
12	Bi residual/Pd (molar ratio)	0.29	0.37	0.35	0.64	0.74
13	Bi/Pd in fresh catalyst (molar ratio determined by XPS)	0.73	0.95	1.56	4.07	12.65
14	Bi/Pd in used catalyst (molar ratio determined by XPS)	0.48	0.49	0.55	0.54	0.53

values are found for the following compositions:

- $0.33 < \mathrm{Bi/Pd} < 0.4$ if Y is normalized with respect to the dissolved bismuth amount (line 10);
- $0.5 < \mathrm{Bi/Pd} < 1$ if Y is normalized with respect to the residual bismuth amount (line 11).

Results qualitatively similar to those displayed in Fig. 2 were already reported several times in the literature in the case of other reactions. Maxima were observed at the following values:

- (Bi/Pt) = 0.1 for the oxidation of sorbose into 2-keto-L-gulonic acid [21];
- (Bi/Pt) = 0.2 for the oxidation of glycerol into dihydroxyacetone [26];
- (Bi/Pd) = 0.1 for the oxidation of lactic acid into pyruvic acid [27];
- (Bi/Pd) = 0.50–0.67 for the oxidation of lactose into lactobionic acid [28];
- (M/Pd) = 0.2 (M = Se, Te, Bi, Sn) in the oxidation of lauric alcohol into lauric acid [7];
- (Pb/Pd) = 4.2 for the oxidation of 1-methoxy-2-propanol into 1-methoxy-2-propanone [29].

As already mentioned in earlier studies [23–25], bismuth was found systematically to dissolve in the reaction medium during the catalytic tests. In contrast with bismuth, palladium dissolution was never detected under the present experimental conditions. As indicated in line 4 of Tables 1–3, bismuth dissolution increases with the Bi/Pd molar ratio. For a given catalyst composition, the percentages of bismuth losses measured after 4 h running are relatively constant whatever the catalyst masses engaged in the experiments. The mean values calculated from line 4 are 11% for **3**Pd**1**Bi/C_0, 10% for **5**Pd**2**Bi/C_0, 32% for **2**Pd**1**Bi/C_0, 38% for **1**Pd**1**Bi/C_0, 55% for **1**Pd**2**Bi/C_0 and 51% for **1**Pd**3**Bi/C_0. For each catalyst, the known difference between the initial and dissolved Bi amounts allowed to determine the residual amount of Bi on the used catalyst. Molar ratios of this residual Bi with respect to Pd could therefore be calculated (Table 1, line 12). This ratio increases with the amount of bismuth initially engaged.

3.1.3. Influence of dissolved bismuth

A monometallic catalyst Pd/C_{SX} has been tested in the presence of increasing amounts of dissolved bismuth according to the procedure described in Section 2.4.3. The catalyst (Bi/C_{SX}) masses engaged in the catalytic tests are listed in Table 2, together with the extent of bismuth dissolved in the reaction medium (expressed as percentages of the initial bismuth load-

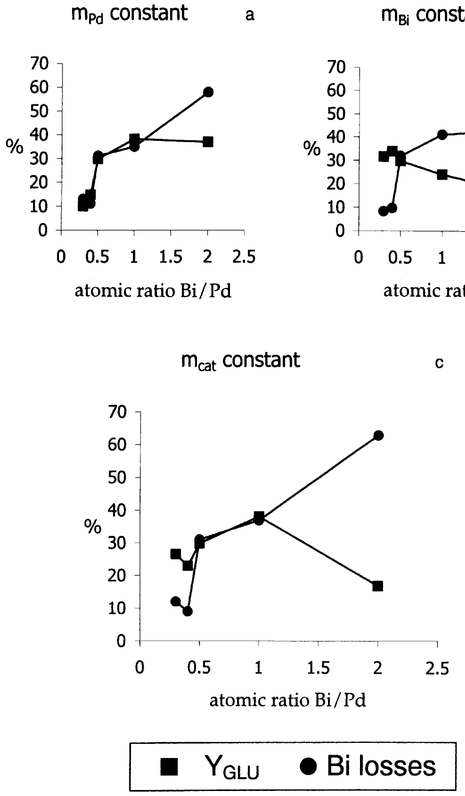

Fig. 2. Yields in gluconic acid and extent of Bi losses vs. catalyst composition for a series of bimetallic **X**Pd**Y**Bi/C_0 catalysts used under standard reaction conditions for 4 h.

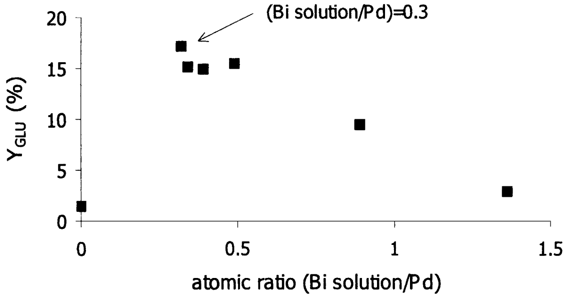

Fig. 3. Influence of the Bi concentration in solution on the yield in gluconic acid obtained with the catalyst Pd/C_{SX} (standard reaction conditions).

ing on the catalyst used for generating this soluble Bi), the masses and concentrations of dissolved bismuth, the molar ratios (Bi total/Pd) and the gluconic acid yields (measured after 2 and 4 h). Fig. 3 shows the gluconic acid yield versus the atomic ratio (dissolved Bi/Pd). These results show that dissolved bismuth promotes the catalytic activity of a monometallic catalyst if the bismuth concentration in the reaction medium is in the range 1.8×10^{-5}–2.8×10^{-5} mol/l. The corresponding Bi/Pd molar ratios are in the range 0.3–0.4, which means an average number of one Bi atom in solution for three Pd atoms on the catalyst. If the bismuth concentration exceeds 2.8×10^{-5} mol/l, the gluconic acid yield decreases. For instance, the

Table 2

Catalytic performances of a monometallic Pd(5 wt.%)/C_{SX} catalyst tested in the presence of soluble Bi generated from a monometallic Bi(5 wt.%)/C_{SX} catalyst

Generation of dissolved bismuth				Catalytic experiment		
m_{cat} (Bi(5 wt.%)/C_{SX}) (mg)	Bi losses (%)[a]	m_{Bi} dissolved (mg)[b]	Bi (mol/l)[c]	Molar ratio (Bi/Pd)	Y_{GLU} (%)[d]	
					2 h	4 h
0	0	0	0	0	1	1
54	74	1.8	1.9×10^{-5}	0.34	8	15
54	71	1.7	1.8×10^{-5}	0.32	9	17
60	77	2.1	2.2×10^{-5}	0.39	7	15
75	76	2.6	2.8×10^{-5}	0.49	9	15
147	71	4.7	5.0×10^{-5}	0.89	5	9
295	54	7.2	7.7×10^{-5}	1.36	2	3

[a] Bismuth losses expressed as percentages of initial bismuth loading on the catalyst used to generate soluble Bi.

[b] Amount of dissolved bismuth engaged in the catalytic measurement.

[c] Bismuth concentration in the reaction medium.

[d] Yield in gluconic acid obtained with the Pd(5 wt.%)/C catalyst (54 mg) in the absence or presence of X mg of dissolved bismuth.

Table 3
XPS atomic intensity ratios in fresh and used ($t = 4$ h) bimetallic Pd–Bi/C catalysts

	Catalyst[a]		Pd/C experimental[b] (×100)	Pd/C theoretical[c] (×100)	Bi/Pd experimental[b]	Bi/Pd theoretical[c]	Bi/C experimental[b] (×100)	Bi/C theoretical[c] (×100)
1	**3**Pd**1**Bi/C_0	Fresh	**2.70**	**0.76**	**0.73**	**0.33**	**1.98**	**0.25**
2		Tested[d]	2.89		0.48		1.38	
3		Tested[e]	2.37		0.48		1.15	
4		Tested[f]	2.81		0.43		1.21	
5	**5**Pd**2**Bi/C_0	Fresh	**2.50**	**0.70**	**0.95**	**0.40**	**2.37**	**0.28**
6		Tested[d]	2.60		0.49		1.30	
7		Tested[e]	2.00		0.53		1.05	
8		Tested[f]	3.00		0.47		1.42	
9	**2**Pd**1**Bi/C_0	Fresh	**2.09**	**0.62**	**1.56**	**0.50**	**3.24**	**0.32**
10		Tested[d]	2.17		0.55		1.20	
11		Tested[e]	2.17		0.55		1.20	
12		Tested[f]	2.17		0.55		1.20	
13	**1**Pd**1**Bi/C_0	Fresh	**0.93**	**0.42**	**4.07**	**1**	**3.79**	**0.42**
14		Tested[d]	2.06		0.54		1.11	
15		Tested[e]	1.57		0.56		0.88	
16		Tested[f]	2.07		0.56		1.16	
17	**1**Pd**2**Bi/C_0	Fresh	**0.32**	**0.25**	**12.65**	**2**	**4.09**	**0.51**
18		Tested[d]	1.35		0.53		0.71	
19		Tested[e]	1.27		0.62		0.80	
20		Tested[f]	0.98		0.64		0.62	
21	**1**Pd**3**Bi/C_0	Fresh	**0.20**	**0.18**	**11.20**	**3**	**2.80**	**0.55**
22		Tested[d]	2.49		0.55		1.36	
23		Tested[e]	0.48		0.56		0.27	
24		Tested[f]	0.69		0.56		0.38	

[a] The catalysts are characterized by different Bi/Pd ratios (bold figures) and by a constant metal/catalyst weight percentage of 10.
[b] Experimental atomic intensity ratio.
[c] Theoretical values of the atomic Pd/C, Bi/C and Bi/Pd ratios calculated from the bulk composition of the catalysts.
[d] Catalyst mass engaged in catalytic test: 54 mg.
[e] Bismuth mass engaged in catalytic test: 2.7 mg.
[f] Palladium mass engaged in catalytic test: 2.7 mg.

yields in gluconic acid measured after 4 h decrease from 15 to 3% if the bismuth concentration increases from 2.8×10^{-5} to 7.7×10^{-5} mol/l. For the latter concentration, the yield in gluconic acid is very close to that of an unpromoted Pd/C catalyst.

3.2. Characterization of the fresh and used supported bimetallic catalysts

3.2.1. X-ray diffraction

Most bimetallic catalysts are characterized by poorly resolved XRD spectra, because of their microcrystalline nature. However, in a few cases, the presence of Bi–Pd intermetallic compounds has been detected in the active phase of bimetallic catalysts [23]. For instance, an intermetallic compound (Bi_2Pd) and metallic bismuth were observed in the catalysts in which the Bi/Pd molar ratio was equal to or higher than 1.

3.2.2. XPS

3.2.2.1. Catalysts used under standard reaction conditions. Representative XPS results are listed in Table 3 for the **X**Pd**Y**Bi/C_0 catalysts before and after their use. Bismuth and palladium appear in the

Table 4
XPS results of **2**Pd**1**Bi/C_{SX} catalyst used in various reaction conditions ($t = 4$ h)

	Reaction medium (substrate–atmosphere)	E_b, Pd $3d_{5/2}$ (eV)	Pd(0)/Pd(II)[a]	Pd/C (×100)[a,b]	Bi/Pd[a,b]	E_b, Bi $4f_{7/2}$ (eV)	Bi(0)/Bi(III)[a]	Bi/C (×100)[a,b]
1	Glucose–O_2	335.9–338.1	2.7	1.12	0.50	158.0–159.7	2.1	0.56
2	Glucose–air	335.7–337.2	3.1	1.05	0.70	157.7–159.0	0.7	0.73
3	Glucose–N_2	335.8–337.7	5.0	1.10	0.82	157.8–159.2	0.7	0.91
4	Gluconate–O_2	335.7–337.8	2.3	1.43	0.38	157.6–159.1	2.3	0.54
5	Gluconate–air	335.7–337.7	2.5	1.17	0.43	157.6–159.2	2.5	0.50
6	Gluconate–N_2	335.7–337.7	3.8	1.22	0.41	157.6–159.2	2.5	0.50
7	O_2	335.7–337.4	2.3	1.29	0.83	157.8–159.0	0.7	1.06
8	Air	335.6–337.3	2.1	1.11	0.90	158.0–159.2	0.8	1.00
9	N_2	335.7–337.5	4.0	1.15	0.86	157.9–159.2	1.3	0.99

[a] Atomic intensity ratios.

[b] Theoretical values of the atomic ratios Pd/C, Bi/C and Bi/Pd calculated from the amounts of Pd, Bi and C used for the preparation: Pd/C (×100) = 0.63; Bi/Pd = 0.51; Bi/C (×100) = 0.32.

metallic (Pd(0), Bi(0)) and the oxidized form (Pd(II), Bi(III)). The binding energy values associated with the Bi $4f_{7/2}$ photopeak lie in the range 157.5–158.0 eV for Bi(0) and 158.8–159.7 eV for Bi(III) and, for the Pd $3d_{5/2}$ line, in the range 335.6–335.8 for Pd(0) and 337.0–337.8 eV for Pd(II).

The experimental surface Bi/Pd ratios in the fresh catalysts are always higher than the theoretical values calculated from the bulk composition of the catalysts. This might be due to a higher dispersion for Bi than for Pd, the latter forming more easily large aggregates. The values could also indicate a partial coverage of palladium by bismuth. In the present case, this observation is in agreement with the sequential incorporation of Pd first, then Bi, during the preparation of these catalysts. It must, however, be mentioned that we obtained the same result independently of the actual preparation procedure of these catalysts, and, in particular, whatever the incorporation sequence of Bi and Pd was.

The atomic intensity ratios Bi/Pd in the used catalysts always decrease due to the bismuth dissolution observed during the catalytic oxidation of glucose to gluconic acid. The ultimate ratio always ranges from 0.4 to 0.6, independently of the initial catalyst compositions and from the extent of bismuth dissolution (mean value of the Bi/Pd ratio of the 18 used catalysts listed in Table 3 is 0.54). These results suggest that bismuth involved in the active phase of the catalyst tends to dissolve until the catalyst surface is characterized by a particular composition, corresponding to two Pd atoms for one Bi atom.

3.2.2.2. Influence of the reaction medium on the surface characteristics of used Pd–Bi/C catalysts. Another series of experiments was carried out with the objective of looking at how the composition of the reaction medium and its evolution during the oxidation reaction could affect the surface state of the bimetallic catalysts. Table 4 presents the XPS data collected with the bimetallic **2**Pd**1**Bi/C_{SX} catalyst engaged in particular tests characterized by various composition of the reaction medium and surrounding atmosphere (air or nitrogen). The surface Bi/Pd ratios in the used catalysts are always smaller when the catalyst was in the presence of gluconate, independently of the atmosphere. Because of its well established complexing properties, gluconate is assumed to enhance Bi dissolution. In addition, the value of the Bi/Pd ratio is constant for the three experiments performed in the presence of gluconate, and equal to 0.4, suggesting once again that this composition does have a direct relevance to the mechanistic model responsible for the synergetic effect.

3.2.2.3. XPS characterization of bimetallic Pd–Bi/C catalysts used in cyclic conditions or long duration experiments. Table 5 summarizes the XPS atomic intensity ratios measured in three different bimetallic Pd–Bi catalysts tested over longer periods, either in

Table 5
XPS results concerning catalysts used for longer reaction times under continuous or discontinuous conditions

	Catalyst		Pd/C (×100)[a,b]	Bi/Pd[a,b]	Bi/C (×100)[a,b]	Pt/C (×100)[a,b]
1	**2**Pd**1**Bi/C_{SX}[c]	Fresh	0.72	1.11	0.80	–
2		Used (1 × 4 h)	1.12	0.50	0.56	–
3		Used (5 × 4 h)	1.19	0.37	0.44	–
4		Used (13 × 4 h)	0.90	0.37	0.33	–
5		Used (1 × 24 h)	1.12	0.42	0.47	–
6	**2**Pd**1**Bi/C_{SX}[c,d]	Used (1 × 24 h)	0.02	0.43	0.09	–
7	Ref/C_{SX}[c,e]	Used (1 × 24 h)	0.91	0.39	0.35	–
8	PdPtBi/C (Degussa)	Fresh	1.06	1.92	2.05	0.24
		Used (1 × 4 h)	1.40	0.75	1.10	0.30
		Used (5 × 4 h)	1.02	0.90	0.92	0.15

[a] Atomic intensity ratios.

[b] Theoretical values of the atomic ratios Pd/C, Bi/C and Bi/Pd calculated from the amounts of Pd, Bi and C used for the preparation: Pd(5 wt.%)Bi(5 wt.%)/C: $\mathrm{Pd/C}\,(\times 100) = 0.63$, $\mathrm{Bi/Pd} = 0.51$, $\mathrm{Bi/C}\,(\times 100) = 0.32$; Pd(4 wt.%)Pt(1 wt.%)Bi(5 wt.%)/C: $\mathrm{Pd/C}\,(\times 100) = 0.50$, $\mathrm{Bi/Pd} = 0.63$, $\mathrm{Bi/C}\,(\times 100) = 0.32$, $\mathrm{Pt/C}(\times 100) = 0.07$.

[c] Support particle size: 100–200 μm.

[d] Catalyst prepared from 2,3-pyrazinedicarboxylate-type precursors (see [23]).

[e] Reference catalyst prepared from $PdCl_2$ and $Bi(NO_3)_3{\cdot}5H_2O$ according to the procedure described in [23].

continuous (24 h) or discontinuous (5 or 13 times, 4 h) conditions. The behavior of a commercial trimetallic Pd(4 wt.%)Pt(1 wt.%) Bi(5 wt.%)/C supplied by Degussa is also reported. It appears that the surface Bi/Pd ratios in the bimetallic catalysts tend to decrease further below 0.6 after running for 24 h or more, the value stabilizing at about 0.4. The trimetallic catalyst behaves differently, the larger stability of Bi in this case being presumably related to the presence of Pt.

3.3. Characterization of fresh and used supported monometallic catalysts

The above series of measurements concerning bimetallic catalysts was completed by a few ones involving monometallic Pd/C catalysts.

3.3.1. X-ray diffraction

Metallic palladium was observed in the fresh and used monometallic catalysts. No bismuth-containing phase was detected in the used Pd/C catalysts tested in the presence of dissolved bismuth.

3.3.2. XPS and SEM-EDX analyses

In contrast with the XRD analyses mentioned above, bismuth has been detected by XPS and SEM-EDX analyses at the surface of the used monometallic Pd/C catalyst tested in the presence of soluble bismuth. These results demonstrate that partial deposition of the dissolved bismuth from the solution occurs onto the surface of the supported monometallic catalyst during the catalytic operations. Bi is assumed to be deposited either on the support or on Pd particles, thereby generating bimetalllic particles of various compositions.

Table 6
XPS atomic intensity ratios in the monometallic catalyst Pd(5 wt.%)/C_{SX} tested in the presence of soluble Bi

Bi concentration of the reaction medium (mol/l)	Pd(0)/Pd(II)	Pd/C (×100)	Bi/Pd	Bi(0)/Bi(III)	Bi/C (×100)
2.2×10^{-5}	1.8	0.65	0.14	1.3	0.09
2.8×10^{-5}	3.5	0.07	0.07	0.7	0.05
5.0×10^{-5}	3.3	0.79	0.09	0.8	0.07
7.7×10^{-5}	2.5	0.06	0.19	0.2	0.01

However, the values of the XPS atomic intensity ratios are too small to draw conclusions concerning the influence of the concentration in soluble bismuth on the extent of the deposition process (Table 6). Bismuth and palladium appear again in the metallic (Pd(0), Bi(0)) and the oxidized form (Pd(II), Bi(III)). These observations differ from those reported earlier on similar experiments performed on fructose oxidation using Bi-promoted Pt/C catalysts, in which X-ray fluorescence failed to detect any Bi deposition on the used catalyst [20].

4. Discussion

Before going further with considerations on the mechanistic scheme according to which bismuth exerts its promoter role, it seems useful to summarize the most relevant experimental facts described above. First, bismuth dissolves partially from the catalyst surface when interacting with the reaction medium, as soon as glucose or gluconate are present. Second, whatever the initial catalyst composition and the extent of Bi dissolution, the molar Bi/Pd ratio measured by XPS at the surface of the used catalysts always appears in the range 0.4–0.6. Finally, Bi introduced in the solution can deposit onto the catalyst surface where it is able to interact with surface Pd atoms.

According to previous investigations, glucose and gluconate present in the reaction medium are both responsible for the bismuth leaching occurring during the catalytic reaction [23]. A similar effect due to the interaction between partially oxidized bismuth and 2-keto-L-gulonic acid has been already reported by Brönnimann et al. [21]. The XPS analyses carried out by Mallat et al. [30] on the evolution of the surface Bi/Pt ratio in Bi–Pt/C catalyst contacted with sorbose under a nitrogen atmosphere also indicated extensive Bi dissolution during the pre-reduction treatment of the catalyst. The authors suggested that the Bi remaining on the Pt surface corresponded to the so-called irreversibly adsorbed species. However, the monometallic and promoted bimetallic catalysts behave very differently with respect to that process. Smits et al. [16] reported some time ago that when Pb-promoted platinum catalysts were put in the presence of gluconic acid under nitrogen, the Pb losses were larger from the monometallic than from the bimetallic catalysts. In the present case, the bismuth losses are also larger from the monometallic Bi/C catalyst than from the corresponding bimetallic Pd–Bi/C catalyst [23]. On the other hand, Besson et al. [31] did not notice any Bi dissolution from Bi–Pd or Bi–Pt catalysts in which the promoter element was selectively deposited on the noble metal at a low Bi loading ($\mathrm{Bi/M} = 0.1, \mathrm{M} = \mathrm{Pd, Pt}$). All these observations go to prove that the dissolved bismuth was initially deposited on the surface of the catalysts as multilayers. Because this kind of bismuth is more readily oxidized than Bi adatoms [8], its dissolution in the presence of strong chelating agents would be easier than that of adsorbed Bi atoms. Considering that Bi is highly insoluble in basic aqueous solution ($K_\mathrm{S}\mathrm{Bi(OH)_3} = 10^{-31}$), the bismuth present in the reaction medium must be complexed by glucose, gluconate or fructose. This aspect will be examined in the next two sections.

Although a similar dissolution phenomenon has been sometimes reported in the literature for the noble metal also, like for Pt in sorbose oxidation [30,32], Pd dissolution from the catalysts was never observed in this work (i.e. Pd concentrations were always below the analytical detection limit corresponding to 10% of the initial Pd amount).

4.1. Bi–gluconate complexes

Whereas details on the synthesis and structural characterization of lead gluconate can be found in an extensive literature dealing with the toxicity of this element [33–37], there have been only few reports on the complexation of bismuth by gluconic acid or gluconate [37,38]. However, a bismuth–gluconate complex described as $\mathrm{BiH_{-2}G{\cdot}H_2O}$,[1] has been recently synthesized and characterized by Frutos et al. [39]. This neutral compound precipitates at 25 °C from an aqueous solution (pH 3.5–9.5) containing the metal and the ligand in a molar ratio ligand/metal equal to 1 or 2. It can be redissolved by further deprotonation of the ligand at high pH. The NMR analysis of the compound formed under these conditions suggests a “2,3,4,5” chelation of the bismuth(III), corresponding to the stoichiometry $[\mathrm{BiH_{-4}G}]^{2-}$. In this complex,

---

[1] In the conventional formulation $\mathrm{H}_{-n}\mathrm{L}^{(n+1)-}$, where *n* represents the number of non-carboxylic protons which have been displaced upon complexation (gluconic acid corresponding to $\mathrm{HLH_4}$).

the carboxylate group which participates in the chelation process at low pH is replaced by ionized sugar hydroxyl groups. A likely interpretation is, therefore, that Bi dissolved in the reaction medium from the supported catalysts is present in solution as $BiH_{-2}G{\cdot}H_2O$ or $[BiH_{-4}G]^{2-}$ compounds.

4.1.1. *Bi–glucose and Bi–fructose complexes*

Metal coordination to carbohydrates has been extensively studied and reviewed by Angyal [40] and more recently by Whitfield et al. [41]. To allow the complex formation to occur in a significant extent, Angyal proposed that three vicinal hydroxyl groups, either in an axial–equatorial–axial (ax–eq–ax) sequence on a 6-membered ring, or in a *cis–cis* sequence on a 5-membered ring, should be present. Complex formation has been identified by NMR spectroscopy, electrophoresis, ion selective electrodes and solubility measurements. In principle, in its pyranose form, D-glucose does not possess this required arrangement of hydroxyl groups. However, several authors [42–44] showed that Ca^{2+} does interact with D-glucose, using electrophoretic measurements, Raman spectroscopy or chromatography. The axial–equatorial (ax–eq) hydroxyl group present as neighbors in the α-D-glucopyranose would be involved in the weak complexation process (compared to those involving sugars having the sequence ax–eq–ax), producing a shift in the anomeric equilibrium of D-glucose. In the same way, complexation of metallic cations by D-fructopyranose would be the result of weak interactions between the cation and either two pairs of ax–eq hydroxyl groups in the β-anomer or one pair of ax–eq group in the α-anomer. Because more adequate sequences are present, fructose is assumed to be a somewhat better complexing agent than glucose. The α-anomer being the major form present in solution, Goulding [44] suggested that α-D-fructopyranose was preferentially involved in chelation and postulated that the exocyclic 1-OH might also contribute to the complexation process when bonding occurs through O(2)O(3). The importance of Bi coordination by D-fructose was also mentioned in experiments dealing with fructose oxidation using Bi–Pt/C catalysts [20]. In addition, the possible involvement of the 5-membered ring furanose forms of glucose and fructose, exhibiting the adequate *cis*-diol moiety, has also to be considered.

Angyal also described the influence of cationic size and charge on the complexation process with D-allose taken as model carbohydrate, in the sense that the α-anomer of this molecule presents the ax–eq–ax arrangement [45]. A first conclusion was that coordination is favored in the case of ions whose Pauling ionic radius is larger than 80 pm, with an optimal value around 100 pm. In addition, for a given ionic radius, the complex stability increases with the ionic charge. With an ionic radius of 96 pm, tervalent Bi^{3+} ions match adequately these requirements.

From the above discussion, we, therefore, suggest that bismuth dissolved from the catalysts in the initial glucose solution or during the early stages of glucose oxidation can be stabilized in solution essentially as a Bi–glucose complex, but eventually also as a Bi–fructose complex provided the fructose concentrations are large enough. The formation of this kind of complex is likely account taken of the formation and the stability of similar compounds between lead and aldopentoses [46]. Coordination would then occur through the two ax–eq hydroxyl groups of α-D-glucose as it was suggested for the Ca^{2+}–glucose complex cited above.

4.2. *Involvement of soluble bismuth*

The promoting effect of dissolved bismuth on a monometallic catalyst Pd/C has been measured for different Bi concentrations in solution (Table 2 and Fig. 3). It appears that soluble bismuth can participate in the promoting effect but, its influence depends on its concentration in the reaction medium. In this way, dissolved bismuth could be responsible for the enhanced catalytic activity of the bimetallic Pd–Bi catalysts. However, we have also shown previously [25] that when a bimetallic or a trimetallic catalyst is engaged in a series of 5 or 13 successive tests, the measured gluconic acid yields remain constant while significant bismuth losses are observed only during the first and the second test. These results suggested first that the catalytic activity was not only determined by the bismuth concentration of the reaction medium, but also that bismuth dissolution was not responsible for catalyst deactivation, or at least not alone. Consequently, most of the dissolved bismuth would represent an excess amount of promoting element which is not necessary to monitor the oxidation reaction, but the presence of small quantities of soluble bismuth in the reaction medium might increase the catalytic activity of these bimetallic catalysts. It can be noticed that the overall shape of Fig. 3 is similar to that observed in lactose oxidation with a catalyst promoted in situ by adding a solution of Bi(III) salt [28]. However, in that case, the catalyst was pre-reduced before its use and the residual amount of soluble Bi should be negligible regarding the reducing ability of lactose. These results, therefore, cannot be directly compared with ours because they actually refer to the activity of a true bimetallic catalyst. Their relevance in terms of mechanistic considerations is furthermore restricted because the involvement of possibly adsorbed molecular species has not been taken into account.

4.3. Surface characteristics of catalysts

Fresh and used bimetallic catalysts have been characterized by XPS. First, in the fresh catalysts, the experimental Bi/Pd ratios are always higher than the theoretical values calculated from the bulk composition of the catalysts, suggesting a partial coverage of palladium by bismuth. Diffusion of metallic bismuth towards the external surface of the active phase can be explained by referring to its lower surface energy compared with palladium [47]. Similar observations were reported at several occasions in papers concerning supported bimetallic catalysts promoted by Pb or Bi [8,21,26]. This behavior is illustrated in Fig. 4. Part (a) refers to the present work and part (b) to a very similar situation reported by Kimura et al. [26] for Bi–Pt catalysts used in the oxidation of glycerol to dihydroxyacetone. Coverage of the noble metal by the promoter element was also confirmed by hydrogen chemisorption experiments [9]. In the present case, this picture is, however, complicated by the fact that the dynamic surface state of the catalyst also involves the interaction between surface Bi atoms and the adsorbed molecular Bi complexes which are characterized by a certain solubility in the reaction medium. Nevertheless, among the two interpretations described above (Section 3.2.2), the one based on coverage of Pd by Bi is in line with literature results and seems the most likely.

Second, in the used catalysts, the surface Bi/Pd molar ratios always decrease in line with the bismuth losses observed during glucose oxidation. A more striking observation lies in the fact that this ratio always reaches a value ranging from 0.4 to 0.6, whatever the initial metallic composition of the catalyst. These results suggest that this particular composition probably plays an important role in the oxidation process. Glucose oxidation might necessitate two or three palladium atoms in association with one Bi atom. This value corresponds nicely to the conclusions derived from pulsed electrochemical techniques applied to determine the number of Pt sites occupied by foreign adatoms [48]. According to these data, the adatoms are arranged on the surface in such a way that they fulfil the valence bond requirements of both the adatoms and the surface Pt atoms. As a consequence, free access to some surface regions is preserved because the adatoms are not closely packed. Within that context, Bi was found to cover three Pd atoms, but

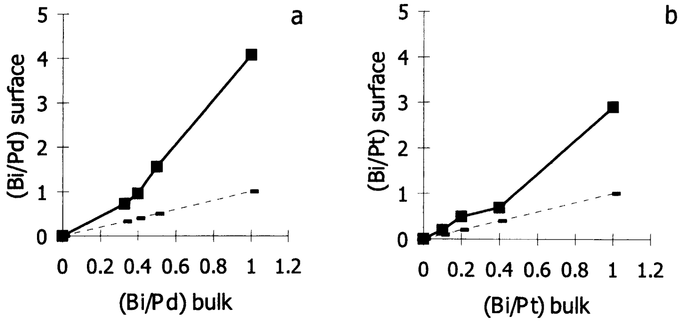

Fig. 4. Comparison between the surface and bulk atomic intensity ratios (a) in bimetallic **X**Pd**Y**Bi/C_0 catalysts and (b) in bimetallic Bi–Pt/C catalysts from [26].

the question whether isolated Bi atoms or molecular Bi complexes are involved remains open.

As far as the binding energies are concerned, the values associated with the Pd $3d_{5/2}$ photopeak vary between 335.4 and 335.9 eV for Pd(0), 336.5 and 338.6 eV for Pd(II). Those associated with the Bi $4f_{7/2}$ photopeak lie in the range 157.5–158.6 eV for Bi(0) and 158.9–160.1 eV for Bi(III). The average dispersion of these values, respectively, 0.4 and 2.1 eV for Pd(0) and Pd(II), 1.1 and 1.2 eV for Bi(0) and Bi(III), are relatively high when taking into account the analytical resolution of the spectrometer (0.2 eV). These variations can be explained by the fact that they refer to metallic states present at the surface of complex catalysts and not to pure metals or oxides. In particular, a continuum of oxidation states can be observed starting from metal atoms interacting with adsorbed oxygen species, up to the formation of true metal oxides. In addition, the residual presence of degradation products resulting from the used metal precursors could also lead to contamination of the signal. The progressive shift in binding energy of the Bi 4f XPS signals has been discussed in detail by Wittstock et al. [49], within the frame of experiments concerning glucose oxidation at Bi-modified Pt electrodes. The lower limit of the BE values for the Bi $4f_{7/2}$ signals corresponds to that assigned by these authors to adsorbed Bi species coordinated to glucose or its oxidation intermediates and products. Furthermore, as reported earlier in the literature for Pd(0) atoms [50], the binding energy can also be modified by the particle size, differences of 0.7 eV being observed between Pd particles of 1.4 and 2.8 nm. On the other hand, there is no detectable promoter influence on the electronic state of Pd, as suggested by the identical binding energy values in the monometallic Pd/C and bimetallic Pd–Bi/C catalysts. Similar conclusions were mentioned for carbon- or alumina-supported Pt–Bi and Pt–Pb catalysts [8,26,51].

4.4. *Composition of the active sites*

We have suggested above that most of the soluble bismuth represents an excess amount of promoting element which is not necessary to ensure optimal catalytic performances. However, we did not exclude the possible promoting effect of a small fraction of this soluble bismuth. We, therefore, suggest that two kinds of bimetallic active sites might be involved in the mechanism of glucose oxidation: (i) active sites formed during the activation step of the bimetallic catalyst and (ii) active sites generated in situ when a monometallic Pd/C catalyst and soluble bismuth are engaged simultaneously in a catalytic test. These two sites will be described hereafter.

4.4.1. *Active sites generated in situ*

Bismuth is obviously not soluble in an alkaline aqueous solution and can be stabilized only in a glucose solution when, it is complexed by the carbohydrate. In the presence of a monometallic Pd/C catalyst, this complex may be adsorbed at the surface of the palladium atoms and undergo an oxidative dehydrogenation reaction (Fig. 5a) according to the mechanism proposed by de Wit et al. [52]. As suggested previously, the oxidation mechanism might necessitate two or three palladium atoms for one bismuth atom. Therefore, the weak activity of a monometallic catalyst tested in the presence of a large amount of

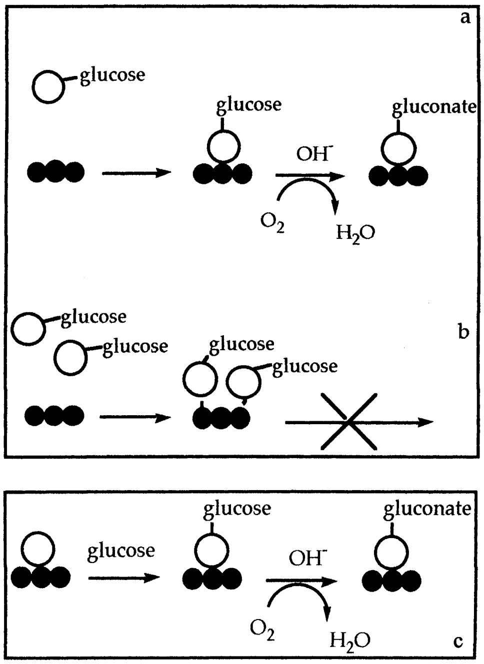

Fig. 5. Mechanistic schemes based on the adsorption of: (a) a Bi–glucose complex at low concentration, (b) a Bi–glucose complex at higher concentration, (c) glucose on pre-formed bimetallic active sites (standard reaction conditions).

dissolved bismuth ($[\mathrm{Bi}] > 7.7 \times 10^{-5}\,\mathrm{mol/l}$) may be attributed to a too extensive adsorption of Bi–glucose complexes on the palladium atoms (Fig. 5b). The XPS and SEM-EDX analyses of the monometallic Pd/C catalyst used in the presence of solubilized bismuth strenghthen this hypothesis since they indicate the presence of adsorbed bismuth on the surface of the used catalyst. However, the surface molar ratios Bi/Pd measured on the corresponding catalysts (Table 6) are small and do not reach the average value classically observed in the range 0.4–0.6 for all bimetallic catalysts after use (Tables 3 and 5). Furthermore, for the experiment performed with the highest Bi concentration in solution, this value is larger (0.19) but the catalyst exhibits a very low activity, which is close to that of the unpromoted catalyst. Clearly, even if Bi(III) reduction by glucose leads to deposition of Bi particles onto the Pd/C catalyst, the activity enhancement observed when such a monometallic catalyst is tested in the presence of soluble Bi cannot be merely explained by the in situ generation of bimetallic Bi–Pd sites that would have the ideal surface stoichiometry. The involvement of the soluble fraction of Bi in the overall mechanistic scheme of glucose oxidation has, therefore, to be considered.

4.4.2. Active sites generated during the activation step

The second kind of bimetallic sites would be created during the activation step of the bimetallic catalyst (heating under a nitrogen flow). Glucose would then be adsorbed at the surface of the bismuth atoms involved in the pre-formed Pd–Bi bimetallic sites and would be submitted to an oxidative dehydrogenation process initiated by the palladium atoms (Fig. 5c). The existence of an optimal Bi/Pd ratio above which the reaction rate decreases or remains constant would, therefore, be attributed to one of the following situations: (i) either a too high coverage of Pd by Bi as suggested by Mallat and co-workers [21] to explain a similar behavior with Pt–Pb/C catalysts in the oxidation of L-sorbose, or (ii) the formation of inactive intermetallic compounds during the activation step of the bimetallic catalysts characterized by high Bi/Pd ratios. The presence of such intermetallics ($\mathrm{BiPd–Bi_2Pd–BiPd_3}$) in the bimetallic catalysts has actually been demonstrated in the course of previous studies, and the catalytic inactivity of one of them, α-$\mathrm{BiPd_3}$, for the selective oxidation of glucose to gluconic acid has been mentioned [24].

4.4.3. Probable nature of the active sites

The two configurations of active sites described in the sections above are actually very close to each other. The first one, corresponding to active sites generated in situ, is the only likely explanation for the fact that the performances of a monometallic Pd/C catalyst, which is essentially inactive in the selected experimental conditions, are significantly improved in the presence of adequate (not too high) amounts of soluble bismuth. In this case, Bi would be initially involved in the active site only as a Bi(III)–glucose complex, and later, as the reaction proceeds, also as a Bi(III)–gluconate complex (and perhaps a Bi(III)–fructose complex). The mild experimental conditions prevailing during the catalytic tests are definitely not adequate to promote the formation of true Bi–Pd alloys or intermetallics at the surface. The second configuration proposed, corresponding to pre-formed bimetallic active sites generated during the activation step under nitrogen, would give rise to two different kinds of surface active sites in operandi: in the first one, zerovalent Bi is stabilized in association with Pd in the form of Bi–Pd alloys, on which both glucose and gluconate can adsorb simultaneously with an oxidation of the promoter to Bi(III) by oxygen; in the second one, a Bi(III)–glucose complex would adsorb on a cluster of three Pd atoms which are not covered by Bi, in a configuration identical to that discussed earlier in the case of monometallic Pd/C catalysts. The relative contributions of these last two mechanisms cannot be evaluated but they undoubtedly depend on the bulk Bi–Pd composition of the bimetallic catalysts and, furthermore, are assumed to change during the course of the oxidation reaction, in relationship with the dynamics of surface modifications associated with the Bi leaching process.

4.5. Promoting role of bismuth

The beneficial effect of bismuth on the activity, selectivity and stability has been clearly demonstrated. As shown by Fig. 6, the addition of bismuth to a monometallic Pd-based catalyst increases significantly the catalytic activity and cancels the catalyst deactivation occurring during the first minutes of a catalytic test.

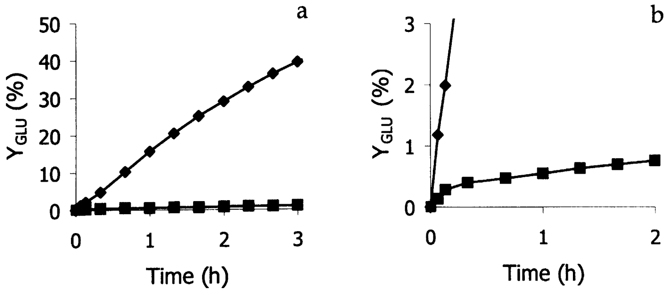

Fig. 6. Yield in gluconic acid vs reaction time under standard conditions: (■) 500 mg monometallic Pd/C_{SX} catalyst (50–100 μm), (◆) 54 mg bimetallic **2**Pd**1**Bi/C_{SX} catalyst (50–100 μm); (a) global curve, (b) expanded scale at low yield in gluconic acid.

4.5.1. *Lessening of catalyst deactivation*

There are three major reasons for catalyst deactivation occurring during liquid phase oxidation of alcohols and aldehydes: (i) by-product formation and its strong adsorption on the active sites, a process which is usually called "chemical poisoning", (ii) overoxidation of the noble metal surface (oxidation of the surface active site M(0) to inactive sites M^{n+}) and (iii) corrosion of the noble metal leading to surface restructuring.

4.5.1.1. Chemical poisoning. This type of poisoning was invoked by several authors in the course of glucose or gluconic acid oxidations [10,16,17,53]. In the present work, ^{13}C-NMR analyses showed that fructose and gluconic acid were the only by-products generated in the reaction medium. When looking at the pH influence on the catalyst deactivation in glucose oxidation, Abbadi and van Bekkum [10] concluded that the phenomenon was restricted essentially to measurements made in acidic media. Even if the formation of other by-products and their irreversible adsorption on the catalyst surface cannot be totally excluded, this hypothesis seems, therefore, unlikely in the present case.

4.5.1.2. Overoxidation. The catalytic reactor works in kinetic regime. Therefore, the oxygen concentration in the reaction medium is rather high, which favors overoxidation of the noble metal surface [1]. In our case, the hypothesis of overoxidation of the catalyst surface is not supported by the Pd(0)/Pd(II) and Bi(0)/Bi(III) molar ratios measured by XPS. However, taking into account that the absolute value of these ratios can be modified upon sampling or under the high vacuum conditions prevailing during the XPS analysis (which could lead to reduction), the occurrence of deactivation phenomena caused by the partial oxidation of the active site can again not be totally excluded.

4.5.1.3. Corrosion and surface restructuring. Palladium has never been detected by atomic absorption in the reaction medium. Therefore, the deactivation of the monometallic Pd/C catalyst cannot be related to the dissolution of the surface active sites.

The two most important interpretations put forward to rationalize the beneficial effect of bismuth on the deactivation process during the catalytic oxidation of alcohols or aldehydes in liquid phase are (i) the geometric blocking effect (a fraction of palladium metal active sites would be blocked by the promoter, resulting thereby in inhibiting the formation and eventual strong adsorption of poisoning species which are assumed to require larger active site ensembles than the target reaction), and (ii) the prevention of oxygen poisoning (bismuth having a higher affinity for oxygen than palladium, it would act as a co-catalyst preventing oxygen poisoning of palladium; in addition, Bi–Pd alloys or intermetallics generated on the surface could be thermodynamically more stable than an association of Pd and Bi oxides or suboxides).

However, the catalytic activity of a monometallic Pd/C catalyst tested in the presence of soluble bismuth does not decrease during a 4 h catalytic run. The coverage of palladium by bismuth in these used catalysts being small (see XPS results, Table 6), the geometric blocking or the higher affinity of bismuth for oxygen cannot be proposed as being responsible for the promoting effect of bismuth. Therefore, the

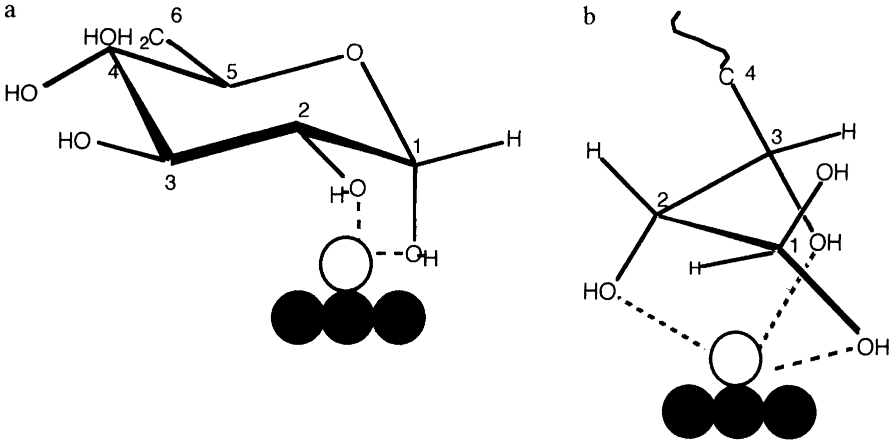

Fig. 7. Two suggested molecular schemes for the Bi–glucose complex generated at the surface of the bimetallic catalyst: (●) Pd, (○) Bi.

lessening of the deactivation phenomenon observed in the bimetallic Pd–Bi/C catalysts could be attributed to an easier desorption of the gluconate from the surface of the catalyst in the presence of bismuth or to an increase of the oxidation rate. When accepting the last explanation, the amount of by-products formed during the catalytic operation and the covering of the catalyst surface by oxygen would decrease, resulting in a lower catalyst deactivation.

4.5.2. Increase of the oxidation rate

The presence of a bismuth–glucose complex at the surface of an active site composed of three palladium atoms and one bismuth atom may facilitate glucose dehydrogenation and consequently increase the oxidation rate. The nature of this complex may be the same as the one described previously in solution. In its pyranose form, α-D-glucose would be coordinated to bismuth through its 1-OH and 2-OH in the cyclic form, or through its 1-OH, 2-OH and 3-OH in the open form (Fig. 7). As mentioned above, coordination through the *cis*-diol moiety of glucofuranose could also occur. The chemical bond formed between bismuth and the 1-OH oxygen atom may facilitate deprotonation of the involved alcohol group and also the subsequent hydride transfer from the carbon atom towards the noble metal surface, according to the mechanism suggested by de Wit et al. [52]. Furthermore, the complexation may bring the 1-H hydrogen atom nearer to palladium, which would make the hydride abstraction by the noble metal definitely easier. The hydride abstraction related to the breaking of the C_1–H bond being the rate determining step, the increase of its rate would increase the global rate of the oxidative process.

5. Conclusions

The partial dissolution of the bismuth initially present at the surface of the bimetallic Pd–Bi/C catalysts ($0.33 <$ molar ratio Bi/Pd < 3; (Bi + Pd)/catalyst $= 10$ wt.%) during catalytic operations has been observed. The pH of the reaction medium being basic, the formation of Bi–glucose or Bi–gluconate complexes in solution is postulated. These complexes may also be generated at the catalyst surface. The complexation process, in solution or at the surface of the catalysts, would facilitate glucose dehydrogenation and, therefore, increase the overall rate of the oxidative process, in line with reduced chemical and oxidative poisoning effects. The complexation process would favor the dehydrogenation reaction either because it allows a better orientation of the substrate molecule towards the noble metal surface, or because the formation of a Bi–O bond (involving the O_1 atom) makes the glucose deprotonation and the subsequent hydride abstraction easier. Furthermore, the formation of a bismuth–gluconate complex may favor the desorption of gluconate from the catalyst surface and consequently reduce the role played by the major reaction product in the catalyst deactivation. The active sites may be composed of one bismuth atom and two or three palladium atoms and the bismuth dissolved in the reaction medium during a catalytic test would be in excess with respect to this composition. Because the concentration of the soluble Bi-complexes with either the reactant or the oxidation product influences the efficiency of the adsorption and desorption processes, the involvement of this soluble fraction of the promoting element in the overall mechanistic scheme of these promoted catalysts is, therefore, suggested in glucose oxidation.

Acknowledgements

The authors greatly acknowledge financial support from the Belgian National Fund for Scientific Research (FNRS, Brussels). They are grateful to NORIT for supplying the carbon supports, to F. Delaruelle, C. Renard and J.F. Statsijns for their assistance in various parts of this work.

References

[1] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[2] P. Gallezot, Catal. Today 37 (1997) 405.
[3] M. Besson, P. Gallezot, Catal. Today 57 (2000) 127.
[4] T. Mallat, Z. Bodnar, A. Baiker, O. Greis, H. Strubig, A. Reller, J. Catal. 142 (1993) 237.
[5] H. Fiege, K. Wedemeyer, Angew. Chem. Int. Ed. Engl. 20 (1981) 783.
[6] M. Hronec, Z. Cvengrosova, J. Kizlink, J. Mol. Catal. 83 (1993) 75.
[7] H. Kimura, A. Kimura, I. Kokubo, T. Wakisaka, Y. Mitsuda, Appl. Catal. A 95 (1993) 143.
[8] T. Mallat, Z. Bodnar, P. Hug, A. Baiker, J. Catal. 153 (1995) 131.
[9] T. Mallat, Z. Bodnar, A. Baiker, in: S.T.H. Oyama, J.W. Hightower (Eds.), Catalytic Selective Oxidation, Vol. 523, American Chemical Society, Washington, DC, 1993, p. 308.
[10] A. Abbadi, H. van Bekkum, J. Mol. Catal. 97 (1995) 111.
[11] T. Mallat, A. Baiker, Appl. Catal. A 79 (1991) 59.
[12] E. Herrero, A. Fernandez-Vega, J.M. Feliu, A. Aldaz, J. Electroanal. Chem. 350 (1993) 73.
[13] T. Mallat, Z. Bodnar, C. Brönnimann, A. Baiker, Stud. Surf. Sci. Catal. 88 (1994) 385.
[14] H. Hayashi, S. Sugiyama, N. Shigemoto, K. Miyaura, S. Tsujino, K. Kawashiro, S. Uemura, Catal. Lett. 19 (1993) 369.
[15] K. Takehira, H. Mimoun, I.S. De Roch, J. Catal. 58 (1979) 155.
[16] P.C.C. Smits, B.F.M. Kuster, K. van der Wiele, H.S. van der Baan, Appl. Catal. 33 (1987) 83.
[17] A. Abbadi, H. van Bekkum, Appl. Catal. A 124 (1995) 409.
[18] P.C.C. Smits, B.F.M. Kuster, K. van der Wiele, H.S. van der Baan, Carbohyd. Res. 153 (1986) 227.
[19] P. Verdeguer, N. Merat, A. Gaset, J. Mol. Catal. 85 (1993) 327.
[20] A.W. Heinen, J.A. Peters, H. van Bekkum, Carbohyd. Res. 304 (1997) 155.
[21] C. Brönnimann, Z. Bodnar, P. Hug, T. Mallat, A. Baiker, J. Catal. 150 (1994) 199.
[22] J.H.J. Kluytmans, A.P. Markusse, B.F.M. Kuster, G.B. Marin, J.C. Schouten, Catal. Today 57 (2000) 143.
[23] M. Wenkin, R. Touillaux, P. Ruiz, B. Delmon, M. Devillers, Appl. Catal. A 148 (1996) 181.
[24] M. Wenkin, C. Renard, P. Ruiz, B. Delmon, M. Devillers, Stud. Surf. Sci. Catal. 108 (1997) 391.
[25] M. Wenkin, C. Renard, P. Ruiz, B. Delmon, M. Devillers, Stud. Surf. Sci. Catal. 110 (1997) 517.
[26] H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, Appl. Catal. A 96 (1993) 217.
[27] T. Tsujino, S. Ohigashi, S. Sugiyama, K. Kawashiro, H. Hayashi, J. Mol. Catal. 71 (1992) 25.
[28] H.E.J. Hendriks, B.F.M. Kuster, G.B. Marin, Carbohyd. Res. 204 (1990) 121.
[29] T.B. Mallat, A. Baiker, Appl. Catal. A 79 (1991) 41.
[30] T. Mallat, C. Brönnimann, A. Baiker, J. Mol. Catal. 117 (1997) 425.
[31] M. Besson, F. Lahmer, P. Gallezot, P. Fuertes, G. Flèche, J. Catal. 152 (1995) 116.
[32] I. Bakos, T. Mallat, A. Baiker, Catal. Lett. 43 (1997) 201.
[33] G.M. Escandar, J.M.S. Peregrin, M.G. Sierra, D. Martino, M. Santoro, A.A. Frutos, S.I. Garcia, G. Labadie, L.F. Sala, Polyhedron 15 (1996) 2251.
[34] T. Lis, Acta Crystallogr. C 40 (1984) 374.
[35] H.A. Tajmir-Rahi, Bull. Chem. Soc. Jpn. 62 (1989) 1281.
[36] R.L. Pecsok, R.S. Juvet, J. Am. Chem. Soc. 78 (1956) 3967.
[37] D.T. Sawyer, J.R. Brannan, Inorg. Chem. 5 (1966) 65.
[38] D.T. Sawyer, Chem. Rev. 64 (1964) 65.
[39] A.A. Frutos, L.F. Sala, G.M. Escandar, M. Devillers, J.M. Salas Peregrin, J.M. Gonzalez Sierra, Polyhedron 18 (1999) 989.
[40] S.J. Angyal, Chem. Soc. Rev. 9 (1980) 415.
[41] D.M. Whitfield, S. Stojkovski, B. Sarkar, Coord. Chem. Rev. 122 (1993) 171.
[42] S.J. Angyal, J.A. Mills, Aust. J. Chem. 32 (1979) 1993.
[43] F. Franks, J.R. Hall, D.E. Irish, K. Norris, Carbohyd. Res. 157 (1986) 53.
[44] R.W. Goulding, J. Chromatogr. 103 (1975) 229.
[45] S.J. Angyal, Pure Appl. Chem. 35 (1973) 131.
[46] L.-G. Ekstrom, A. Olin, Acta Chem. Scand. A 31 (1977) 838.
[47] A.R. Miedema, Z. Metall. 69 (1978) 287.
[48] N. Furuya, S. Motoo, J. Electroanal. Chem. 98 (1979) 189.
[49] G. Wittstock, A. Strübing, R. Szargan, G. Werner, J. Electroanal. Chem. 444 (1998) 61.
[50] J.C. Bertolini, P. Delichere, B.C. Khandra, J. Massardier, C. Noupa, B. Tardy, Catal. Lett. 6 (1990) 215.

[51] H. Hayashi, S. Sugiyama, Y. Katayama, K. Kawashiro, N. Shigemoto, J. Mol. Catal. 91 (1994) 129.

[52] G. de Wit, J.J. de Vlieger, A.C. Kock-van Dalen, R. Heus, R. Laroy, A.J. van Hengstum, A.P.G. Kieboom, H. van Bekkum, Carbohyd. Res. 91 (1981) 125.

[53] J.M.H. Dirkx, H.S. van der Baan, J.M.A. Van den Broek, Carbohyd. Res. 59 (1977) 63.

[54] M. Besson, P. Gallezot, in: R.A. Sheldon, H. van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley/VCH, New York/Weinheim, 2001, pp. 491, 507.